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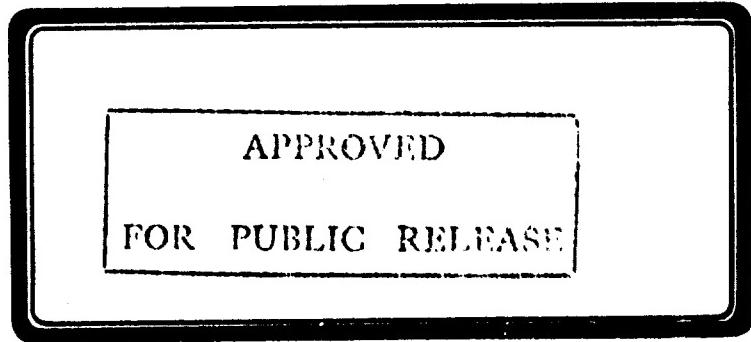
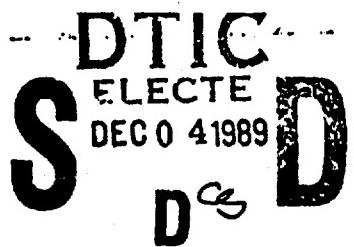
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A PRELIMINARY ASSESSMENT OF NTO AS AN  
INSENSITIVE HIGH EXPLOSIVE

(4)

R. J. SPEAR, C. N. LOUEY AND M. G. WOLFSON



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A PRELIMINARY ASSESSMENT OF  
3-NITRO-1,2,4-TRIAZOL-5-ONE (NTO) AS AN INSENSITIVE HIGH EXPLOSIVE

R.J. Spear, C.N. Louey  
and M.G. Wolfson

MRL Technical Report  
MRL-TR-89-18

ABSTRACT

A simple two-step method to produce NTO in high yield from semicarbazide hydrochloride has been defined. A free-flowing material with bulk density 0.9 g/ml has been produced by stirred aqueous recrystallisation; surfactants were ineffective in altering crystal habit. Impact sensitiveness of NTO was higher than expected although apparent propagation ability is low. Ignitability under thermal and electrostatic stimuli is substantially lower than RDX. Experimental firings were conducted to assess explosive performance for charges pressed to about 90 %TMD; velocity of detonation at 12.7 mm and 15.9 mm diameter was determined while detonation pressure (plate dent) and critical diameter were estimated. Performance at these diameters is somewhat lower than RDX. Moulding powders for 95:5 NTO/binder formulations were prepared from three commercial EVA resins and a flame retardant polyphosphazene. All three NTO/EVA formulations were insensitive to impact. Recommendations for continuing studies on insensitive booster formulations have been made.

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**A PRELIMINARY ASSESSMENT OF  
3-NITRO-1,2,4-TRIAZOL-5-ONE (NTO) AS AN INSENSITIVE HIGH EXPLOSIVE**

1. INTRODUCTION

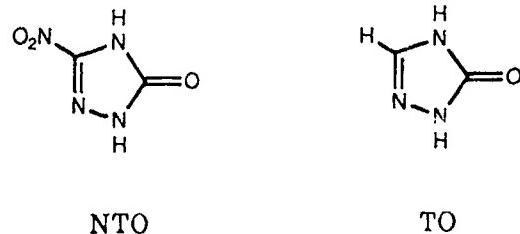
Over the past decade the military Services of the Western nations have increasingly moved toward adopting policies requiring munitions to be insensitive (invulnerable) to unplanned hazardous stimuli. Foremost in this regard has been the United States Navy (USN), which has a clear policy that all on-board munitions will be insensitive by 1995 [1, 2]. While the attainment of insensitivity criteria will require a number of factors to be addressed such as system design, mitigation devices and storage configurations, a key component is decreased sensitivity of the explosive fillings.

Two principal approaches have been used to decrease the sensitivity of explosive fillings while maintaining (or in some cases enhancing) performance.

- i. The use of cast-cured polymer bonded explosives (PBXs) formulated from high performance explosives such as RDX and HMX and a rubbery or thermoplastic polymer binder [3]. PBX main charges typically exhibit substantially reduced vulnerability to hazardous stimuli, and in many weapons systems permit attainment of technical requirements for insensitive munitions (IM) [4].
- ii. The use of very insensitive explosives such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), either alone or with other explosives such as RDX, in combination with a relatively low polymeric binder. The insensitive explosive modifies the charge hazard response to achieve the desired degree of invulnerability.

As yet the Australian Services have not adopted an official policy on IM, although it is currently under active consideration [5]. Technology base R & D on insensitive explosive fillings is being carried out at MRL principally on cast-cured PBXs for warheads and pressed PBXs for fuze boosters, but also in other areas such as less sensitive melt cast TNT formulations. A wide range of polymeric binders, explosive fillers and formulation methods are being examined.

One candidate insensitive high explosive filler is 3-nitro-1,2,4-triazol-5-one (NTO). NTO was first reported in 1905 [6] from nitration of 1,2,4-triazol-5-one (TO).<sup>\*</sup> There was renewed interest in NTO in the mid-late 1980s [7-9], but none of these nor



subsequent chemical studies [10] appear to be directed to explosives. It was not till 1985 that Coburn and Lee [11] published the first study on NTO as an explosive. However, as early as 1980 it was known that the French were working on a "new insensitive high explosive", which was subsequently revealed in 1987 to be NTO [12, 13]. During a visit by one of the authors (RJS) to the UK in late 1986 it was suggested that the French were marketing an HMX/NTO/binder cast-cured PBX; certainly formulations of this type are covered by the patent [12] and the ICT technical presentation [13]. The US also recently developed an NTO based insensitive formulation [14], and some additional information was gained during a visit by Mr M.A. Parry of MRL to the US in mid-1988.

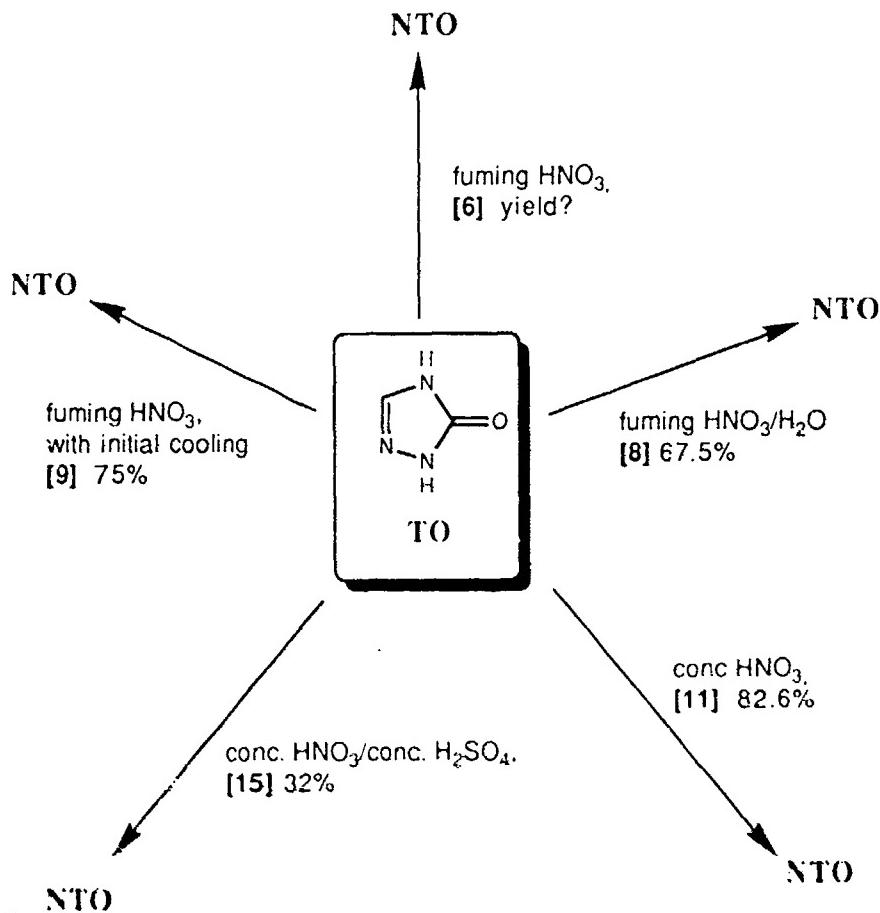
NTO should have good potential for Australian use since it can be produced in a simple two-step process from readily available starting materials. In addition, a future weapons system considered for Australian procurement could have an NTO based warhead filling. As part of the technology base R & D on explosives, it was decided to undertake a preliminary assessment of NTO, which forms the basis of this report. The subjects addressed were preparation of NTO in good yield in a form suitable for formulation, characterisation of sensitiveness and thermal properties, a limited assessment of explosive performance and preparation of some NTO-based PBXs. Recommendations on continuing evaluation as part of our insensitive munitions tasking are made.

## 2. PREPARATION OF NTO

Manchot and Noll [6] prepared NTO by reaction of 1,2,4-triazol-5-one (TO) and fuming nitric acid, although few specific details were given. Kräger et al [9] used this earlier procedure, with TO (1.31 g) being treated with fuming nitric acid (5-6 ml) initially with cooling and subsequently at room temperature; a yield of 75% (based on TO) was claimed. Gehlen and Schmidt [7] also used the Manchot and Noll [6] method, although no details were given, but Chipen et al [8] report that this gave only carbonization. Their optimum method was TO (10 g), fuming nitric acid (15 ml) and water (8 ml), heated till reaction commenced

\* Manchot and Noll [6] incorrectly attributed NTO to be the hydroxy tautomer 5-hydroxy-3-nitro-1,2,4-triazole.

as noted by vigorous evolution of  $N_2O_4$ , then removing from the heat source to give 10.4 g (67.5% yield). Katritzky and Ogrétir [15] reported nitration of TO with mixed conc. sulfuric-nitric acids (3:1) but yields of NTO were low (32%). Lee et al [11] prepared NTO by nitration of TO with conc. nitric acid and claimed a yield of 82.6% based on TO. A summary of these various preparations is shown below in Scheme 1.

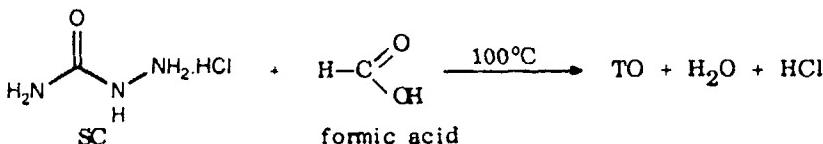


Scheme 1. Published methods for preparation of NTO from TO

One major aim of this study was to identify, using scheme 1 as a starting point, experimental conditions for preparation of NTO in high yield and purity. This required firstly a decision on the best method for preparation of TO, which has been reported using a number of procedures including reaction of acetone semicarbazone with formic acid [8], or semicarbazide hydrochloride (SC) with formic acid [8, 11] or triethylorthoformate [15]. Chipen et al [8] concluded from the methods that they studied that the SC-formic acid procedure was the best, while Lee et al [11] also used this procedure in a one pot system, i.e. TO was not purified but was subsequently nitrated to NTO which was then purified.

It was decided, on the basis of the above published data, to use the SC-formic acid method (shown below in Scheme 2), to prepare TO. In addition, it was also decided to use as a starting point the 'one-pot' procedure of Lee et al [11] whereby the TO was not

isolated and purified but was instead nitrated directly with conc. nitric acid using the same reaction vessel.



Scheme 2. Preparation of TO by condensation of semicarbazide hydrochloride (SC) and formic acid

### 2.1 Nitrations using Conc. Nitric Acid

The initial preparations of NTO were carried out on 1/20th of the scale described in the report of Lee et al [11], with only the temperature for the nitration reaction being varied. The results of these experiments are detailed in Table 1, preps 1-10. A further two experiments (preps 11, 12) were carried out using a smaller volume of conc. nitric acid (125 ml cf. 155 ml in the standard procedure). Neither the purity of the TO nor the % conversion from the SC was determined, but each experiment was carried out on unrecrystallised TO prepared in an identical manner.

In the first experiments (preps 1-5), the reaction vessel was heated with stirring on a hot-plate/stirrer to a set internal temperature, then removed from the heat and placed on a metal bench, i.e. with no external heating. This method was chosen as it appeared to most closely resemble that described by Lee et al [11]. These few experiments identified two variables as being very important.

- i. If the reaction is heated to an excessive initial temperature ( $73^{\circ}\text{C}$ , prep 1), the internal temperature rises to well over  $100^{\circ}\text{C}$  and yield of NTO is poor. This most likely results from either hydrolysis of NTO, which has been shown to occur in 51.6%  $\text{H}_2\text{SO}_4$  at  $130^{\circ}\text{C}$  [7] and 73.3 - 98.35%  $\text{H}_2\text{SO}_4$  at  $70^{\circ}\text{C}$  [15], or alternatively from oxidation by the nitric acid [8].
- ii. If the reaction mixture is heated to too low a temperature ( $59^{\circ}\text{C}$ , prep 2), a low conversion results due to inadequate temperature rise. This could have been overcome by continuing the reaction for a longer time, but this option was not investigated.

Because of variability in the yields and difficulty in carrying out the reactions in these first experiments, the remaining preparations were all conducted with the reaction flask immersed in a water bath set to an initial temperature. These are detailed in preps 6-10.

Prep 7 again (cf prep 1) demonstrates the undesirability of excessive reaction temperature. In this series of preparations the optimum yield was 75.3% obtained for a bath temperature of  $65^{\circ}\text{C}$ , an internal temperature maximum of  $82^{\circ}\text{C}$ , and a reaction time of 2 h (prep 9). Longer reaction time (prep 10) or lower bath temperature (preps 6, 8) decreased NTO yield. Decrease in the volume of nitric acid (preps 11, 12) also decreased yield.

## 2.2 Nitrations using Mixed Acids

Using 65°C as the optimum initial reaction temperature, a series of preparations were carried out using mixed acids, i.e. replacing some of the conc. nitric acid with conc. sulfuric acid or fuming nitric acid. Results are detailed in Table 2.

Using either 125 ml (prep 1) or 100 ml (prep 3) of conc. nitric acid with 20 ml of conc. sulfuric acid gave the highest yields of this study (> 77%). Increase in reaction time (compare preps 1 and 2, 3 and 4) decreased yield. The nitrations catalysed by sulfuric acid were in general more vigorous, and often accompanied by some foaming, than those with conc. nitric acid alone, while maximum temperatures were higher and reached in a shorter time. Use of fuming nitric acid (prep 5) appeared to offer no advantage.

## 2.3 Scaled-up Reactions

Three scaled up reactions (133.8 g SC) were carried out at the optimum temperature (65°C) using conc. nitric (Table 1, preps 13, 14) or mixed nitric/sulfuric acids (Table 2, prep 6). All experiments gave substantially lower yields than expected. This was probably due to either the excessive reaction times (the dependence on reaction time noted above had not yet been realised) or alternatively that conversion of SC to TO may not have proceeded to the same extent on the larger scale of reaction.

## 2.4 Recommendation on Preparative Method

Reaction of SC with formic acid followed by nitration with mixed nitric/sulfuric acid at a reaction temperature of 65°C has been identified as an excellent preparative procedure giving NTO in high yield in a simple one-pot procedure. Further experiments need to be carried out to define the optimum reaction conditions, particularly with respect to reaction time. A procedure to determine the extent of conversion of SC to TO also needs to be established.

## 3. VARIATION OF NTO CRYSTAL HABIT

The products obtained from the above reactions tend to acicular crystal habit with length/diameter ratios in excess of 3:1. Micrographs of some typical examples are shown in Fig 1a and b. This material had relatively poor handling properties, particularly flow. In order to alter crystal habit and enhance flow and bulk density, two approaches were investigated.

### 3.1 Crystal Modification using Surfactants

Surfactants are frequently used to alter the crystal habit of explosives during crystallisation/purification. This particularly applies to primary explosives and high explosives of high polarity (high dipole moments) such as nitroglycerine (NG) [16] where improved handling properties through increased bulk density and flow can be achieved. NTO, like NG, has a quite high polarity and should be amenable to alteration of crystal properties by use of surfactants.

Recrystallisation of NTO from water was carried out in the presence of a number of neutral, anionic and cationic surfactants:

- i. Neutral : gelatin, methyl cellulose, coconut diethanolamide (Diamond Shamrock), phospholan PDB-3 (Diamond Shamrock)
- ii. Anionic : aerosol OT (BDH), orotan 960 (Rohm and Haas)
- iii. Cationic : cetyl ammonium bromide (BDH)

Small scale crystallisations (approximately 0.5 g NTO/5 ml H<sub>2</sub>O at 100°C) were carried out without stirring and using both fast and slow cooling rates. Typical surfactant concentrations were about 1% although both higher and lower concentrations were investigated for some systems.

The general trend observed for these crystallisations was that the acicular habit tended to be accentuated, i.e. the opposite to that desired. Only gelatin gave some improvement in crystal and bulk properties, while methyl cellulose gave NTO agglomerated into a semi-granular form. The effect of gelatin and methyl cellulose was therefore further investigated on a larger scale (2.5 g NTO/25 ml H<sub>2</sub>O). Both crystallisations were carried out without stirring using 1% aqueous surfactant solution.

Gelatin produced circular clumps of crystals. These clumps could be easily broken up to individual crystals as shown in Fig. 2a. There was some improvement in handling properties over unrecrystallised NTO. The product crystallised from methyl cellulose consisted of balled agglomerates of microfine NTO needles (Fig. 2b). Handling properties were poor.

A final larger scale recrystallisation (20 g NTO/200 ml 1% aqueous gelatin) was carried out with stirring (see following section). However the NTO product was quite acicular in habit (cf Fig. 1) and exhibited poor handling properties.

At this stage an aqueous crystallisation method which produced NTO with desirable handling properties had been developed, and work on crystal modification by surfactants was terminated. In summary, all surfactants tested favoured acicular growth of NTO. Different crystal modifiers such as inorganic salts may have been beneficial, and they could be evaluated in the future.

### 3.2 Aqueous Crystallisation with Stirring

Small scale aqueous recrystallisation experiments were carried out in parallel with the surfactant experiments described in the previous section. Scale up to 26.2 g NTO/225 ml H<sub>2</sub>O without stirring and allowing the flask to cool to room temperature followed by refrigeration overnight gave NTO where the bulk crystals were largely irregular in shape (Fig. 3a) with reasonable handling properties. However, a number of 'cubic' crystals (Fig. 3b) could be seen adhering to the flask in a ring above the bulk NTO crystals. Repetition on the same scale showed this behaviour to be reproducible.

Previous studies at MRI, particularly for preparation of spherical NQ, had demonstrated the benefits of stirring with an anchor blade stirrer during crystallisation [17]. A batch of NTO (23.35 g/200 ml H<sub>2</sub>O) was recrystallised with stirring via an anchor blade stirrer both during the dissolution and cooling phases. Crystallisation was completed by overnight refrigeration without stirring. The product obtained showed good handling properties.

A larger scale batch (67.6 g/650 ml H<sub>2</sub>O) was prepared using an identical procedure. The product had a bulk density of 1.055 g/ml and exhibited good flow; physical properties were qualitatively assessed as equivalent to Grade A RDX. A photomicrograph of some typical crystals is shown in Fig. 3c. A series of recrystallisations were then carried out on scales up to 88.9 g NTO/900 ml H<sub>2</sub>O; the results are detailed in Table 3, preps 3-9. The previous two experiments described above are listed as preps 1 and 2.

The results in Table 3 show the following.

1. Recrystallisation typically achieved  $\approx$  90% recovery based on cm<sup>3</sup> NTO.
2. The bulk density was typically  $\approx$  0.9 g/ml. Three preparations had bulk density  $>$  1.0 g/ml but in two cases it was  $\approx$  0.8 g/ml.
3. The crystal form of all products was comparable with that depicted in Fig. 3c; the two examples with lower bulk density had noticeable numbers of crystals tending to acicular habit.
4. No attempt was made to produce NTO of any particular particle size. In all cases, except prep 2,  $>$  90% of product consisted of particles  $<$  850  $\mu$ m.

The method is quite sensitive to changes from contamination or adverse experimental conditions. For example, prep 7 was inadvertently left unattended and the water boiled down to about 400 ml. The NTO product obtained after addition of further water and preparing in the usual manner was yellowish, contained more fine particles than usual and had lower bulk density than the almost identically prepared preps 8 and 9. A possible explanation is formation of hydrolysis products which lead to changes in crystal size and habit distribution.

A second example was another crystallisation where about 20% of gelatin modified NTO was added to the impure NTO. In addition not all the NTO was dissolved prior to cooling. The recrystallised NTO was definitely inferior to that in preps 1-9, Table 3. Presumably even the small amount of gelatin introduced by this process was detrimental. The effect of not completely dissolving the NTO possibly resulted in seeding from these undissolved acicular crystals to give an increase in the undesired acicular form.

#### 4. CHARACTERISATION OF NTO

##### 4.1 Solubility

Solubility of NTO was determined in water at three temperatures: 4.85°C (refrigerator), 18.95°C (ambient temperature) and 43.3°C. In addition, solubility was determined at 18.95°C in acetone, ethyl acetate and dichloromethane, chosen as representative of solvents which could be used in formulation studies with polymers. Results are detailed in Table 4.

Solubility of NTO in either water or acetone is less than 2% at ambient temperature, rising to about 10% in water at 100°C. Solubility in either ethyl acetate or dichloromethane is low; this will facilitate formulation with polymers using solvent-based processes.

## 4.2 Sensitiveness

Sensitiveness to mechanical impact, thermal and electrostatic stimuli was determined on loose crystals for both unrecrystallised and recrystallised NTO. Data are detailed in Table 5; US and French data for NTO and RDX [11-13, 18], and MRL data for RDX are given for comparison.

### 4.2.1 Impact Sensitiveness

Rotter impact sensitiveness was determined on a total of five NTO samples: three recrystallised and two unrecrystallised (Table 5). The F of I values are equal to or slightly higher than RDX for the recrystallised samples (indicating equal or slightly decreased sensitiveness) and lower for the unrecrystallised NTO except in one case (F of I 90) where a very powdery sample was tested.

These results are surprising when compared to the US data (Table 5), particularly that from Lee and Coburn [11]. The NSWC data [18] are consistent with sensitiveness equal to TNT, i.e. very significantly less than RDX. French data [13] also support this conclusion. Note that the MRL value for average evolved gas for ignition is 3-6 ml (Table 5) compared to RDX which is typically > 15 ml. The evolved gas is generally considered to be a measure of ease of propagation [19], hence we would classify NTO as a material which ignites relatively easily but propagates poorly. The US data, where the criterion for ignition depends significantly on propagation (flash, bang etc), not surprisingly rates NTO as relatively insensitive.

The comparison between MRL Rotter impact data and US data for a number of "insensitive" high explosives has shown a similar trend to that observed here for NTO. The relationship between Rotter impact data and "insensitivity" is currently being further investigated at MRL.

### 4.2.2 Thermal Sensitivity

Vacuum thermal stability testing at 120°C resulted in no detectable gas evolution from NTO. Thermal stability of NTO is thus considerably better than RDX and this is confirmed by the higher ignition temperature (T of I) and DSC/DTA exotherm temperature (Table 5). The decrease in T of I for the recrystallised NTO relative to the unrecrystallised NTO is surprising and requires further confirmation. US and French data (Table 5) are consistent with the MRL data.

The decreased energy output of NTO relative to RDX can be seen from the heats of reaction (Table 5). This difference will be accentuated by the very small samples used for DSC/DTA determination owing to the poor ability of NTO to propagate; this difference would be expected to decrease substantially for higher masses under the extreme conditions of detonation.

### 4.2.3 Electrostatic Spark Sensitivity

No ignitions were obtained for NTO at the highest test energy (4.5 J). This can be contrasted with RDX which ignites at 4.5 J but not at 0.45 J. US measurements (Table 5) where energies for initiation are actually determined, give a better comparison.

#### 4.3 Explosive Properties

The explosive performance data that have been published on NTO [11-13, 18] are collated in Table 6. Although informative in containing some measurements of detonation velocity (VOD) and pressure ( $P_{CJ}$ ), in most instances they lack supporting information such as confinement, charge diameter and/or density, or initiation system, and their usefulness is therefore limited. Further data are available on NTO/nitramine/binder formulations [12-14, 18] and, while providing good comparison with corresponding TATB/nitramine/binder formulations, they also suffer from the limitations of the NTO data described above and are not presented here.

In order to provide an initial data base of NTO explosive performance, a series of firings was conducted on NTO charges pressed in all except one case to about 90 %TMD (theoretical maximum density) corresponding to a density of  $1.737 \text{ Mg/m}^3$ . Diameters used were 12.7 and 15.9 mm and both unconfined and confined charges were tested. Full details are listed in Table 7.

The principal information sought was:

1. Estimation of critical diameter
2. Determination of VOD
3. Comparative plate dent performance with currently used explosives

The firings on 12.7 mm diameter NTO showed that detonation can be achieved at this diameter at 91.0 %TMD. This confirms the results of Lee and Coburn [11], who also observed failure at 94.5 %TMD for 12.7 mm diameter (Table 6). NTO will not pick up directly from an exploding bridgewire detonator (EBW) but requires a booster; in this case RDX at 90 %TMD was used.

VOD was determined on confined 12.7 mm charges pressed to 89.61 and 89.76 %TMD, and a 15.9 mm charge pressed to 88.65 %TMD (Table 7). VOD for the 12.7 mm charges was relatively low at around 6000 m/s, with poor ionisation probe output and high standard deviation. This could have been due to long run distances to detonation, i.e. velocity varied appreciably over the charge length, or that detonation was unstable. The 15.9 mm charge gave a VOD of 7440 m/s with a standard deviation of 125 m/s, indicating that stable detonation had been achieved.

Analysis of the data in Tables 6 and 7 suggests that the critical diameter of NTO may be close to 12.7 mm at 90 %TMD, particularly since the detonations observed on confined charges at 12.7 mm diameter indicated potential instability. A provisional estimate for unconfined critical diameter is  $11 \pm 2 \text{ mm}$  at 90 %TMD.

Plate dents, while not an ideal method of measuring detonation pressure, can be used as a rough indicator of relative detonation pressures. The results for plate dent volume give NTO pressure output as 85% (at 12.7 mm diameter) and 88.5% (at 15.9 mm diameter) relative to tetryl, and 76% relative to RDX at diameter 12.7 mm (Table 7). The substantially higher critical diameter of NTO (RDX and tetryl critical diameters are typically < 2 mm) [20a] will decrease the performance of NTO relative to RDX and tetryl at these diameters. At larger diameters NTO performance approaches that of RDX [18].

- 
- This potentially conflicts with the data in the previous paragraph. Longer unconfined 12.7 mm charges should be fired and VOD determined so that detonation stability can be confirmed.

Clearly use of NTO in a booster formulation would require the addition of a shock sensitive explosive such as RDX or HMX to improve performance at small diameters. However the shock sensitivity of NTO as measured on the large scale gap test is substantially higher than TATB (Table 6) [13] and there should be advantages for an NTO/RDX formulation relative to an "insensitive" booster formulation such as PBXW-7 (RDX/TATB/Viton A 85:60:5).

Assessment of the utility of NTO as a main charge explosive requires further experimental determination of VOD and  $P_{CJ}$ , particularly at larger diameters.

## 5. NTO MOULDING POWDERS

In published studies NTO has been assessed as an explosive filler in cast-cured main charge fillings [12-14], moulding powders for pressed fillings [12] and cast composite propellants [12]. One potential area for future assessment at MRL was the incorporation of NTO into pressed fillings for boosters; the insensitivity to mechanical and thermal stimuli would be expected to substantially decrease hazard response relative to currently used booster explosives.

Moulding powders are usually prepared by the solvent slurry process [20b, 21] whereby the solid explosive, mechanically agitated as an aqueous slurry at typically 60-95°C, is treated with a solution of polymer in a volatile solvent. The solvent is evaporated under reduced pressure, precipitating the polymer which coats the explosive crystals and forms granules.

The water solubility of NTO precludes use of this method; uncoated crystals would crystallise out on cooling. The method described in the French patent [12] requires NTO to be stirred with a solution of polymer in solvent (the specific example cited is for Kel-F 800 in ethyl acetate), then the solvent is removed under vacuum. This method is undesirable since it requires stirring of dry explosive lightly coated with polymer at the completion of solvent evaporation.

An investigation was accordingly carried out to derive a method for coating NTO with a range of polymers. A suitable method was found to be to dissolve the polymer in a suitable solvent to a concentration of 10% w/v, then to add this solution to NTO and stir the suspension while chilled in ice water. A solvent in which the polymer has low solubility was then added to precipitate the polymer onto the NTO crystals to form granules. The product was finally isolated by filtration under vacuum.

Three ethylene-vinyl acetate (EVA) polymers; Elvax 650 (11-13% vinyl acetate (VA)), Elvax 210 (27.2-28.8% VA) and Levapren 408 (40% VA), and a flame retardant polyphosphazene; Ethyl Corp. PZX-42 Masterbatch, were studied. For each polymer 95:5 NTO-polymer formulations were prepared using a range of solvents. The optimum solvent combination was defined as the one which gave the moulding powder with the best handling properties; these are listed for each formulation in Table 8. All moulding powders produced by these optimum processes were reasonably free flowing with the exception of the Levapren 408 formulation which was sticky with a strong tendency to clump. A flow modifier such as zinc stearate would be necessary to produce desirable handling properties for this formulation.

Rötter F of I values were determined for these formulations and are listed in Table 8. All the EVA based polymers strongly desensitised the NTO to impact; all had  $F \text{ of } I > 200$ . In contrast the polyphosphazene yielded only a slight desensitisation, with the

F of I being 95 compared to 90 for the least sensitive NTO sample (Table 5). Inhibition of propagation was achieved as evidenced by the lower average gas evolution relative to NTO (2.2 versus 3-6 ml).

Ignition temperatures (T of I) were little changed from the NTO crystals that the formulations were made from. The higher T of I for the polyphosphazene could be attributed to this polymer, which is a flame retardant, but would need further experimental substantiation. This is currently being investigated for polyphosphazene formulations with other high explosive crystals.

Scanning electron micrographs of uncoated NTO crystals and polymer coated crystals are shown in Fig. 4. NTO crystals coated with EVA polymers (Figs 4b, c) show an uneven coating of deposited polymer. It is suggested that the parallel etched exposed surface is due to partial dissolution of the NTO during polymer deposition. Although the EVA coating is significantly poorer than for comparable RDX formulations [22], it is apparently sufficient to give the very high F of I. In contrast to the EVA compositions, the polyphosphazene formulation had only small amounts of polymer deposition (Fig. 4d) as well as minimal crystal dissolution. As a consequence this polymer had only a marginal desensitisation effect, although propagation was reduced.

In summary the results look very promising for producing an insensitive booster or main charge formulation. Charge hazard response would need to be assessed to confirm desirable mild output under cook-off and other threats.

## 6. EXPERIMENTAL

### 6.1 Materials

Semicarbazide hydrochloride was laboratory grade purchased from BDH. Formic acid was AR grade, 88%, purchased from Ajax Chemicals. Nitric acid, 70% w/w (Ajax Chemicals), sulfuric acid, specific gravity 1.84 (BDH) and nitric acid, 100% (Merck) were all AR grade.

Celatin (Ajax Chemicals) and methyl cellulose (BDH) were available from previous studies. Aerosol OT and cetyl ammonium bromide were purchased from BDH. Coconut diethanolamide and phospholan PDB-3 (Diamond Shamrock) and Orotan 960 (Rohm and Haas) were samples kindly donated by the Australian subsidiaries.

Eivax 650 and 210 (Du Pont), Levapren 468 (Bayer) and Polyphosphazene PZX-42 Masterbatch (Ethyl Corp) were samples kindly donated by the Australian subsidiaries.

Distilled water was used in all cases. Solvents used for solubility determinations were "P" grade and for formulation studies were laboratory grade.

### 6.2 Preparation of 3-Nitro-1,2,4-triazol-5-one (NTO)

#### 1,2,4-Triazol-5-one (TO)

Formic acid (88%, 34.5 ml) was added in one portion to semicarbazide hydrochloride (33.45 g) in a 500 ml Erlenmeyer flask at ambient temperature. The mixture was heated with stirring (hot plate magnetic stirrer/surrounding water bath) at 80°C for 2 h, when dissolution was complete and evolution of HCl had ceased. The magnetic stirrer was

removed from the flask, then the contents were taken down to dryness on a rotary evaporator (bath temperature about 70°C). Water (50 ml) was then added and the crude TO was again reduced to dryness.

The flask was left unstoppered at room temperature. The nitration to NTO was generally performed within 48 h. The three larger scale reactions were performed at three times this scale in a 1 l flask.

Recrystallisation of a sample from water (approximately 1.5 ml/g) gave TO as creamy crystals, mp 232-234°C (yield 75-85%). Further sublimation or a second recrystallisation from water raised the mp to 234-235°C, lit. [7] mp 234-235°C.

#### Nitration of TO

The procedure described below is the one which gave the maximum yield. Other variations on this method using different nitration agents and bath temperatures are detailed in Tables 1 and 2. Earlier preparations where only the initial reaction temperature was controlled (Table 1, preps 1-5) were carried out by heating with stirring then removing from the hot plate and allowing to stand on a bench at ambient temperature.

The 500 ml Erlenmeyer flask containing the crude TO (from the preparation described above) was placed in a water bath preheated to 65°C on a hot plate stirrer. A magnetic follower was added followed by a mixture of conc. nitric acid (100 ml) and conc. sulfuric acid (20 ml). The internal temperature rose to a maximum of 86°C after 8 min. Water bath temperature was controlled by addition of ice water; a maximum of 66.5°C was recorded. After 1.5 h the flask was removed from the water bath, allowed to cool to about 30°C internal temperature then finally chilled in ice water. The NTO was isolated by filtration under suction and the crude product was washed with ice water (20 ml) then allowed to dry at the pump overnight. Yield of NTO was 30.30 g (77.0% ex semicarbazide hydrochloride).

Larger scale reactions (Table 1 preps 13 and 14, Table 2 prep 6) were carried out as described above except a 2 l beaker was the reaction vessel, a larger water bath was used and reaction times were longer (see Tables).

### 6.3 Crystal Modification of NTO

#### Recrystallisation with Surfactants

Aqueous surfactant solutions were made by adding the surfactant to water to form an approximately 1% solution. In some cases heating was used to facilitate dissolution. Higher concentrations were also investigated in a number of cases.

The general procedure was to add 5 ml of the surfactant solution to NTO (0.5 g) in a 10 ml Erlenmeyer flask. The contents were heated to 100°C to effect dissolution then allowed to cool. NTO isolated by filtration under vacuum was then examined by microscopy.

Scaled up preparations (2.5 g/25 ml 1% aqueous surfactant) in 50 ml Erlenmeyer flasks were carried out for gelatin and methyl cellulose. A further scale up was carried out for NTO (20 g) in 1% aqueous gelatin (200 ml) in a 500 ml beaker using stirring during dissolution and cooling (as described below).

#### Aqueous Recrystallisation with Stirring

NTO (80.3 g) and distilled water (800 ml) were placed in a 1 l beaker on an electrically heated hot plate. The flask was heated while the contents were stirred with a teflon anchor blade stirrer (dimensions 7.6 cm wide, 0.9-1.9 cm high) driven by an overhead stirrer motor at about 60 rpm. After complete dissolution at 100°C (in some experiments additional water had to be added) heating was stopped and stirring continued till ambient temperature was reached. The beaker was removed and refrigerated overnight. The NTO was then recovered using filtration under suction and finally dried at the pump.

#### 6.4 Material Characterisation of NTO

##### Microscopy

Optical microscopy was performed using a Leitz Ortholux microscope. Photomicrographs were taken with a Leitz Orthomat 35 mm automatic camera on polaroid film type 667. Magnifications in all cases were X42.

##### Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using a Cambridge Instruments Model S250 Mk II scanning electron microscope with a tungsten electron gun. The instrument was operated at 20 kV in the secondary electron mode. Samples of HNS were mounted on a stub coated with PVA adhesive and sputter coated with a conducting film of gold. The micrographs were normally obtained for tilt angles of 20-30 degrees.

##### Sieve Sizing

The dried NTO obtained from aqueous recrystallisation (Table 3) was passed through two Endecott 20 cm diameter sieves, 1.4 mm then 850  $\mu\text{m}$  pore size, using gentle brushing. Material retained on each sieve was removed and weighed.

##### Bulk Density

The NTO passing through the 850  $\mu\text{m}$  sieve into the collection pan (usually 60-80 g and constituting the bulk of the crystallisation product; see Table 3) was transferred to a 100 ml graduated cylinder and the accurate mass was noted. The cylinder was tapped on the bench about 20 times and allowed to settle. This procedure was repeated at hourly intervals till constant volume had been achieved. The bulk density was determined as mass NTO divided by final volume, i.e. g/ml.

##### Solubility

An accurately weighed amount (4 decimal places) of NTO was added to a 25 ml volumetric flask and solvent added to the line. The flask was held at the desired temperature for at least a week. Excess NTO was recovered by filtration and its mass accurately determined. If all the NTO dissolved, a second portion was added and again allowed to stand for one week. All determinations were carried out in duplicate or triplicate.

## **6.5 Determination of Explosive Sensitivity of NTO**

### **Rotter Impact Sensitiveness [19, 23a]**

Impact sensitiveness was determined using a Rotter apparatus. The sample of about 30 mg confined in a brass cap fitted over a polished steel anvil was impacted by a 5 kg weight falling from a preset height. Go/no-go was delineated by > 1 ml gas evolution from the sample for a positive result. Impact heights were varied in a typical Bruceton procedure [24] with a total of 50 caps being tested. The resulting Figure of Insensitiveness (F of I) is quoted relative to RDX Grade G = 80 and is rounded to the nearest 5 units. Gas evolution represents the average for all positive results. In the case of the NTO/EVA formulation, no ignitions were observed at maximum drop height (F of I > 200).

### **Temperature of Ignition [23b]**

Temperature of Ignition (T of I) was determined using an instrument built to specification for the ERDE T of I test. Samples of 200 mg in glass test tubes were heated at 5°C/min till ignition occurred. Ignition was defined by either visible signals such as smoke/flame or audible hiss/bang. The T of I is the temperature at which this event occurred and is the average of duplicate samples.

### **Vacuum Thermal Stability [25]**

The test procedure consisted of placing duplicate 5 g samples in glass sample tubes, attaching to a mercury filled manometer and evacuating. The sample tubes were then placed in a heated bath at 120°C, and a 1.5 h period allowed for temperature equilibrium. The volume of gas evolved was then monitored for 40 h. The quoted result is gas evolved in ml/5 g at 120°C for 40 h and is the average of duplicate samples.

### **Differential Scanning Calorimetry (DSC)**

DSC thermograms were recorded using a Perkin Elmer DSC-2 Differential Scanning Calorimeter equipped with a Scanning Auto Zero accessory. Experimental conditions were as follows: a flowing nitrogen atmosphere (15 ml/min), a heating rate of 5°C/min, and aluminium lids placed, but not crimped, on the pans. The thermograms were recorded using an identical but empty aluminium pan as reference.

### **Electric Spark Test [23c]**

The test procedure consists of filling the sample into a 6.35 mm diameter hole in a polythene strip backed by a copper foil electrode, then enclosing the top with a second foil electrode. The energy from a capacitor connected to the two electrodes is then discharged through the sample. Testing commences using a 0.1 µF capacitor charged to give an output of 4.5 J. If any discharge results in ignition, defined as explosion or consumption of the sample, a new sample is then re-tested using a 0.01 µF capacitor charged to give an output of 0.45 J. Passage of the spark through the sample normally results in some localised charring, particularly at 4.5 J. The samples are inspected after 10 discharges and replaced if charring is excessive. A non-ignition requires that 50 discharges have not resulted in ignition.

## 6.6 Explosive Performance Testing

Pellets for explosive testing were pressed in hardened steel moulds using an Instron Universal Testing machine adjusted to operate as a press [26]. Densities were determined by accurate dimensional measurement and weight.

### Non-instrumented Firings

For non-instrumented firings a pressed cylindrical test charge was positioned in the centre of a mild steel witness block, 75 mm diameter x 25 mm thick. The charge was initiated axially either directly by a UK Mk 3 exploding bridgewire detonator (EBW), or via a tetryl or RDX booster charge placed on top. For confined firings the test charge and booster charge were fitted into a brass sleeve having an outside diameter of 25.4 mm.

Detonation or non-detonation was assessed by whether or not a sharply defined dent was observed in the witness block. Dent volumes were determined by filling the crater with modelling clay, taking care to avoid trapped air and scraping flush with the top edges of the crater. Witness blocks were weighed before and after filling to determine the mass of modelling clay. Density of the clay sample was determined by water displacement, then the dent volumes were calculated.

Approximate dent depth measurements were made using a dial gauge. The dial gauge was first zeroed 5 mm in from the outside edge of witness plate, which was supported on an aluminium anulus to minimise the effect of distortion of the base of the witness plate. By placing the dial gauge probe into the dent and slowly moving the witness plate, the maximum depth of dent was measured. Three measurements were made for each plate. It should be noted that this was not meant to be a rigorous dent test.

### Instrumented Firings : VOD Measurements

A schematic of the system used is shown in Figure 5. The explosive assembly was similar to that used for the uninstrumented firings except that a number of small holes were drilled in the brass confining tube where the NTO pellet would be positioned. Prior to insertion of the explosive pellets ionisation probes were stuck into the holes with their ends flush with the bore of the tube. For the 12.7 mm diameter firings, one tetryl and one NTO pellet was used; the EBW detonator fitted slightly into the confining sleeve. The 15.9 mm diameter firing was conducted using two NTO pellets and one tetryl booster pellet, which only partially fitted into the brass confining tube.

The two 12.7 mm diameter firings were carried out with 5 ionisation probes; 4 were fitted into the holes in the brass confining tube and one parallel foil probe was sandwiched between the base of the NTO charge and the witness block. In one shot, twisted wire ionisation probes were fitted in the probe holes and for the other, a single insulated wire was fitted in each hole, with a common wire being connected to the tube. The latter method was tried because of difficulties encountered with twisted wire probes shorting during fitting. In both cases probes were connected to capacitor discharge pulse circuits and the resultant pulses were captured on a digitising oscilloscope. Inter-probe times were then measured using the oscilloscope cursors. Hard copies of the probe pulses were produced using the plotter (Fig. 5).

The firings on 15.9 mm diameter charges differed in that 6 ionisation probes were fitted into holes drilled into the tube over the length of the last NTO pellet, with a seventh probe at the base of the charge, i.e. no readings were obtained on the first NTO pellet.

The assemblies were fired on mild steel witness blocks. All charges produced dents indicative of detonation. The depths and volumes of the dents were also measured for the 12.7 mm diameter charges.

The mean VOD and standard deviation were calculated using a linear regression. As can be seen (Table 7) the standard deviations for the 12.7 mm firings are very high and therefore the VOD figures should be treated with some caution. The 15.9 mm firing gave a clean, consistent output with acceptable standard deviation.

#### NTO Moulding Powders

##### NTO/Polyphosphazene (95:5)

NTO (9.5 g) was added to a flask containing polyphosphazene PZX-42 Masterbatch in cyclohexane (10% w/w, 5 g) at ambient temperature. Extra cyclohexane (5 ml) was added, the flask was cooled in an ice bath and stirring commenced using an anchor blade stirrer driven by an overhead air motor. Isopropanol (25 ml) was added dropwise over a period of 2-3 min, followed by a further 10 ml added all at once. Stirring was continued for a further 5 min then the product was isolated by filtration under suction following by drying under suction.

Solvent combinations for the NTO/ethylene vinyl acetate formulations which were prepared in a similar manner to the above, are listed in Table 8.

#### 7. SUMMARY

A preliminary assessment of production, explosive hazard and performance of the insensitive high explosive 3-nitro-1,2,4-triazol-5-one (NTO) has been undertaken. A method has been derived to produce NTO in high yield (> 77% based on semicarbazide hydrochloride as feedstock) in a simple two step reaction. It is considered that this yield could be improved if further study on reaction conditions (temperature, reaction time, nitration medium) was undertaken, particularly with respect to scaling up.

Bulk handling properties of the NTO have been improved using a stirred aqueous recrystallisation method, which increased bulk density to > 0.9 g/ml. Optimisation of particle size range was not attempted and would require additional development studies. Surfactants were ineffective in improving crystal habit/bulk density, although additional effort using different types of modifiers could lead to improvements.

NTO in the powder/crystal form has impact sensitiveness equal to tetryl. This was unexpectedly high since US published data rate NTO as less sensitive than TNT; the difference is suggested to result primarily from the differing assessment methods (Rotter vs ERL machines) and particularly to defining go/no-go. Explosiveness, as assessed through ease of propagation, appears to be low but charge hazard tests should be conducted to further define this parameter. Ignitability under thermal stimuli is significantly decreased relative to RDX, as is sensitivity to electrostatic stimuli.

Published data on explosive performance of NTO has been reviewed. A series of experimental firings on unconfined and confined 12.7 mm and 15.9 mm diameter charges pressed to about 90 %TMD were carried out. It has been estimated that the unconfined critical diameter is 11 : 3 mm at 90 %TMD. Effective detonation requires boosting and

NTO will not detonate directly from an EBW detonator. Velocity of detonation of 90%TMD confined charges at 12.7 mm diameter was relatively low at around 6000 m/s and gave evidence of unsteady behaviour. Detonation was increased to 7440 m/s at diameter 15.9 mm and appeared to be stable. Relative detonation pressure as measured by plate dent paralleled the VOD results, being about 85% and 76% of tetryl and RDX respectively at 12.7 mm diameter, and an increased percentage at 15.9 mm diameter.

Accurate solubilities of NTO in water, acetone, ethylacetate and dichloromethane were measured. The solubility in water precluded preparation of PBX moulding powders using an aqueous slurry method, and solvent/non-solvent precipitation methods were derived for four commercial polymers; three ethylene-vinyl acetate (EVA) copolymers, and a polyphosphazene which had flame retardant properties. NTO polymers formed moulding granules with the EVA polymers (ratio 95:5) which were very impact insensitive. In contrast NTO/polyphosphazene (95:5) was slightly desensitised relative to NTO but propagation ability was decreased.

Studies should continue on the use of polymer coated NTO in an insensitive booster explosive formulation. Performance measurements on NTO (see above) suggest that addition of a shock sensitive explosive such as RDX or HMX would be necessary to give the required performance at small diameters. The results observed here are promising and would be needed to be backed up by charge hazard tests, particularly for cook-off. Investigation of an insensitive main charge filling based on NTO could also have strong potential but the larger quantities of NTO which would be required would significantly increase the technical risk and difficulty.

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TABLE I  
PREPARATION OF MTO FROM SEMICARBAZIDE HYDROCHLORIDE (SC)/FORMIC ACID/CONC.  
NITRIC ACID IN ONE-POT REACTION UNDER VARIOUS CONDITIONS

Prep	SC (g)	Formic Acid (ml)	Conc. $\text{HNO}_3$ (ml)	Method	Max Temp at time (°C)	time (min)	Yield <sup>a</sup> (g) (%)
1	33.45	34.5	155	Heat flask with stirring on hot-plate to 73°C, remove and leave standing at room temperature	106.5	10	17.98 45.7
2	33.45	34.5	155	As 1, heated only to 59°C, put back on heat, heat to 100°C	65 100	23.35 22.89 <sup>c</sup> 58.2	b
3	33.45	34.5	155	As 1, heat to 66°C	66		
4	33.45	34.5	155	As 1, heat to 70.5°C	84	10	26.35 67.0
5	33.45	34.5	155	As 1, heat to 72°C	98	11	24.53 62.3
6	33.45	34.5	155	Flask stirred, held in bath at 60°C for 6 h	75	30	26.87 68.3
7	33.45	34.5	155	Flask stirred, held in bath at 72.5°C. After 9 min interval temp had reached 106°C, flask was removed and placed in a cool spot	108	9	14.26 36.2
8	33.45	34.5	155	Flask stirred, held in bath at 62°C for 6 h	74	25	26.53 67.4
9	33.45	34.5	155	Flask stirred, held in bath at 65°C for 2 h	82	16	29.62 75.3
10	33.45	34.5	155	Repeat of 9 but reaction time 3 h	85	17	27.88 70.8
11	33.45	34.5	125	Flask stirred, held in bath at 65°C for 1 h	84	23	26.13 66.4
12	33.45	34.5	125	Repeat of 11 but reaction time 2 h	79	20	26.64 67.7
13	133.8	138.0	620	Flask stirred, held in bath at 65°C for 5.5 h	92.1	20	88.53 56.3
14	133.8	138.0	620	As for 12 but reaction time 6.5 h	100.0	19	77.2 49.1

<sup>a</sup> Yields are based on SC

<sup>b</sup> No product formed

<sup>c</sup> Total from three crops recovered from filtrate

TABLE 2

PREPARATION OF NTO FROM SEMICARBAMIDE HYDROCHLORIDE (SC) / FORMIC ACID/MIXED  
ACID IN ONE POT REACTION AT 65 °C

Prep	SC (g)	NITRATION CONDITIONS				Method	Max temp (°C)	time (min)	Yield (%)
		Formic Acid (ml)	HNO <sub>3</sub> (ml)	H <sub>2</sub> SO <sub>4</sub> (ml)	Fuming HNO <sub>3</sub> (ml)				
1	33.45	34.5	125	20		Flask stirred, held in bath at 65 °C for 1.5 h	86	18	30.30 77.0
2	33.45	34.5	125	20		As for 1 but reaction time 2.25 h	98	9	28.90 73.4
3	33.45	34.5	100	20		As for 1 but reaction time 1 h 40 min	104	7	30.47 77.4
4	33.45	34.5	100	10		As for 1 but reaction time 2.5 h	92	13	28.44 72.3
5	33.45	34.5	75		25	As for 1	101	11	27.50 69.9
6	133.8	138.0	500	80		Flask stirred, held in bath at 65 °C for 8 h	105	7	88.88 56.5

\* Yields are based on SC.

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TABLE 3

MTO AQUEOUS RECRYSTALLISATION<sup>a</sup> WITH STIRRING TO OPTIMISE BULK PROPERTIES

PREP	Mass MTO (g) <sup>a</sup>	Volume H <sub>2</sub> O (approx. ml) <sup>b</sup>	YIELD PURE MTO			PARTICLE SIZE DISTRIBUTION			BULK DENSITY OF SUB 850 $\mu\text{m}$ MATERIAL (g/ml)	
			(g)	(%) <sup>c</sup>	< 850 $\mu\text{m}$	> 850 $\mu\text{m}$ but < 1.4 mm	< 1.4 mm	nd	nd	nd
1	23.35	200	21.1	90.5	nd	nd	nd	nd	nd	nd
2	67.6	650	61.2	91.4	46.8	13.4	nd	nd	nd	1.055
3	80.3	800	71.3	88.8	69.2	1.8 <sup>d</sup>	nd	nd	nd	0.70
4	85.0	850	77.7	91.4	73.3	3.5 <sup>e</sup>	nd	nd	nd	1.045
5	85.0	870	76.3	89.8	68.7	6.6	nd	nd	nd	0.90
6	82.5	880	71.3	86.4	69.6	1.5	nd	nd	nd	0.80
7	88.5	850 (ex Prep 13, Table 1)	79.8	90.1	78.5	-1	nd	nd	nd	0.88
8	88.9	900 (ex Prep 6, Table 2)	79.8	89.8	75.3	4.0	nd	nd	nd	1.015
9	77.2	850 (ex Prep 14, Table 1)	72.3	92.7	71.6	-0.2	nd	nd	nd	0.96

<sup>a</sup> MTO was material ex reactions detailed in Tables 1 and 2, plus earlier preparations not reported.<sup>b</sup> At 100 °C.<sup>c</sup> Based on mass of crude MTO which was recrystallised.<sup>d</sup> In most cases no crystals, or only a few, were retained on the 1.4 mm sieve (see footnote e).<sup>e</sup> Approx. 1 g was retained on the 1.4 mm sieve.

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TABLE 4

SOLUBILITY OF NTO IN WATER, AT A RANGE OF TEMPERATURES, AND  
ACETONE, ETHYL ACETATE AND DICHLOROMETHANE AT AMBIENT (18.95°C) TEMPERATURE

	Solubility in g/100 ml at temperature below			
	4.05°C	18.95°C	43.3°C	100°C
Water	0.72	1.28	2.6	approx. 10 <sup>a</sup>
Acetone		1.68		
Ethyl acetate		0.28		
Dichloromethane		< 0.02		

a Estimated from recrystallisation investigations

TABLE 5

IMPACT SENSITIVENESS, THERMAL AND ELECTROSTATIC SENSITIVITY DATA FOR NTO. PUBLISHED DATA AND DATA FOR RDX ARE SHOWN FOR COMPARISON

Test	NTO Data	
	Recrystallised	Unrecrystallised
<b>IMPACT SENSITIVITY</b>		
MRL data: Rotter F of I (mean gas evolved, ml) <sup>a</sup>	90(3), 80(5)	75(6), 70(6)
	RDX = 80(17)	90(5)
US data: $h_{50\%}$ (cm) <sup>b</sup>	291 (RDX = 22) <sup>c</sup>	75-104 (RDX = 15-20) <sup>d</sup>
French data (J) <sup>e</sup>	22 (RDX = 4.5)	
<b>THERMAL SENSITIVITY</b>		
Vacuum thermal stability		
MRL data (ml/g/120°C/40 h)	0.0 (RDX = 0.2-0.6)	
US data (ml/g/120°C/48 h) <sup>c</sup>	0.3 (RDX = 0.12-0.9)	
Ignition temperature		
MRL data: T of I (°C)	258, 258 (RDX = 216 ± 3)	270, 270, 280
US data: Henkin Critical Temp. (°C, 0.64 mm) <sup>c</sup>	237 (RDX = 219.6)	
French data: T of I (°C) <sup>e</sup>	290 (RDX = 220)	
DSC/DTA exotherm		
MRL data: DSC (°C at 5°C/min heating rate)	273 (RDX = 212)	
Heat of decomposition (kJ/g)	1.76 (RDX = 2.78)	
US data: DTA (°C)	> 236 (RDX = 210) <sup>c</sup>	
	270-275 (RDX = 230) <sup>d</sup>	
<b>ELECTROSTATIC SENSITIVITY</b>		
MRL data (J)	> 4.5 (no ignition)	> 4.5 (no ignition)
	RDX 4.5 ignition	
	0.45 no ignition	
US data (10 ml), J <sup>c</sup>	3.40 (RDX = 0.55)	

<sup>a</sup> Mean of evolved gas readings for all ignitions (defined as > 1 ml)

<sup>b</sup> Drop height (in cm) for 50% ignition probability

<sup>c</sup> Data from reference [11]

<sup>d</sup> Data from reference [10]

<sup>e</sup> Data from references [12, 13]

TABLE 6

PUBLISHED EXPERIMENTAL RESULTS FOR EXPLOSIVE  
PERFORMANCE OF NTO

Experimental Firing	Result	Reference
Density $1.781 \text{ Mg/m}^3$ (92.2 %TMD) at 41.3 mm diam <sup>a</sup>	$P_{CJ}$ 27.8 GPa	11
1.854 (96.0) 41.3	26.0	
1.782 (92.3) 25.4	24.0	
1.855 (96.1) 25.4	Failed	
1.759 (91.1) 12.7	$P_{CJ}$ 25.0 GPa	
1.824 (94.5) 12.7	Failed	
Density $1.91 \text{ Mg/m}^3$ b	VOD 8590 m/s	13
Charges of various density b	VOD 7700-8670 m/s $P_{CJ}$ 31.0-34.0 GPa	18
Density $1.69 \text{ Mg/m}^3$ in 4 mm o.d. copper sheath	VOD 7400	12
1.71	VOD 7770	
NOL large scale gap test (density not stated)	$m_{50\%}$ 260 cards RDX = 310, TATB = 190	13

a Presumed to be unconfined but not stated in (11)

b No further details given

TABLE 7

EXPERIMENTAL FIRINGS OF PRESSED NTO CHARGES. RESULTS FOR TETRYL AND RDX PLATE DENTS ARE INCLUDED FOR COMPARISON

Donor Charge (%TMD) <sup>a</sup>	Acceptor Charge (%TMD) <sup>b</sup>	Charge Diam. (mm)	Confinement (mm)	Result for Acceptor Charge
EBW	NTO (88.5)	12.7	None	Non-detonation
EBW	NTO (75.5)	12.7	None	Non-detonation
EBW/RDX (90.0)	NTO (91.0)	12.7	None	Detonation
EBW	NTO (90.4)	12.7	Brass, 25.4 o.d.	Non-detonation
EBW/tetryl (90.6)	NTO (89.8)	12.7	Brass, 25.4 o.d.	Detonation
EBW/tetryl (88.7)	NTO (89.8)	12.7	Brass, 25.4 o.d.	Detonation: plate dent 3.37 mm deep, volume 1.02 ml
EBW/tetryl (88.7)	Tetryl (89.7)	12.7	Brass, 25.4 o.d.	Detonation: plate dent 3.42 mm deep, volume 1.20 ml
EBW/tetryl (88.6)	RDX (90.0)	12.7	Brass, 25.4 o.d.	Detonation: plate dent 4.03 mm deep, volume 1.35 ml
EBW/tetryl (88.7)	NTO (89.61)	12.7	Brass, 25.4 o.d.	VOD 6,040 m/s (s.d. 700)
EBW/tetryl (88.8)	NTO (89.61)	12.7	Brass, 25.4 o.d.	VOD 5,670 m/s (s.d. 490)
EBW/tetryl (90.0)	NTO (89.24)	15.9	None	Detonation
EBW/tetryl (90.0)	NTO (89.74)	15.9	Brass, 25.4 o.d.	Detonation: plate dent 4.14 mm deep, volume 3.13 ml
EBW/tetryl (90.0)	Tetryl (90.0)	15.9	Brass, 25.4 o.d.	Detonation: plate dent 4.57 mm deep, volume 3.54 ml
EBW/tetryl (90.0)	NTO (88.65)	15.9	Brass, 25.4 o.d.	VOD 7440 m/s (s.d. 125)

a UK Mk 3 exploding bridgewire detonator with a single booster pellet, diameter same as acceptor charge, where stated.

b Single pellet, height approximately equal to charge diameter, except for last entry where two pellets of NTO were used.

TABLE 8

PREPARATION METHODS AND SENSITIVITY DATA FOR 95:5 NTO-POLYMER  
FORMULATIONS STUDIED

POLYMER	MOLDING POWDER	SENSITIVITY DATA	
	PREPARATION METHOD Solvent/non-solvent	ROTTER F OF I <sup>a</sup> (gas evolved, ml)	T OF I (°C)
Elvax 650 (Du Pont, 11-13% vinyl acetate)	toluene/cyclohexane	> 200	
Elvax 210 (Du Pont, 27.2-28.8% vinyl acetate)	ethyl acetate/methanol	> 200	254, 254
Lovapren 408 (Bayer, 40% vinyl acetate)	ethyl acetate/methanol	> 200	
Polyphosphazene PZX-42 Masterbatch (Ethyl Corp.)	cyclohexane/isopropanol	95 (2.2)	260, 260

<sup>a</sup> Relative to RDX grade G = 80



Figure 1 Photomicrographs of unrecrystallised NTO obtained from the nitration of TO, showing the typical acicular crystal habit (X42).

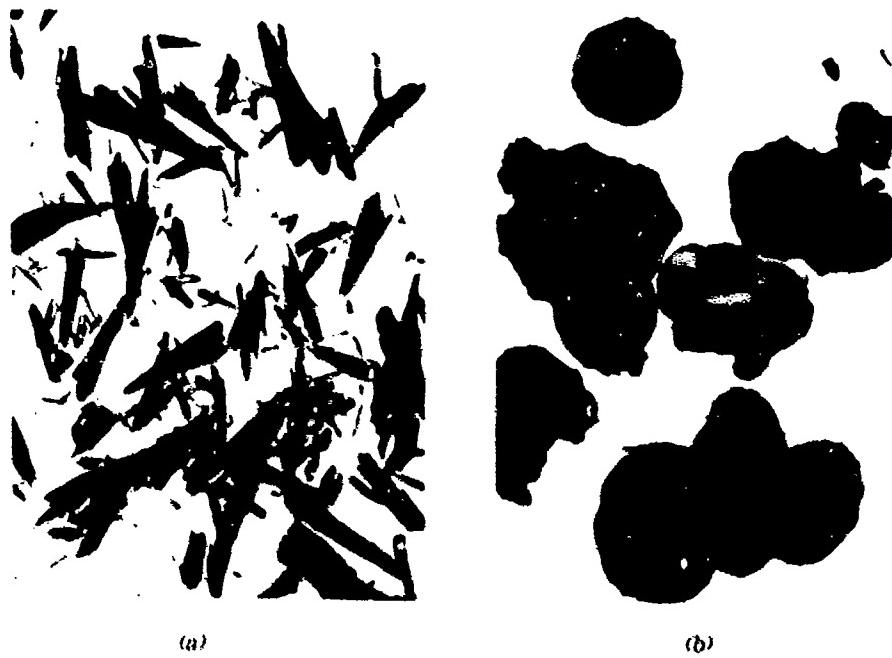
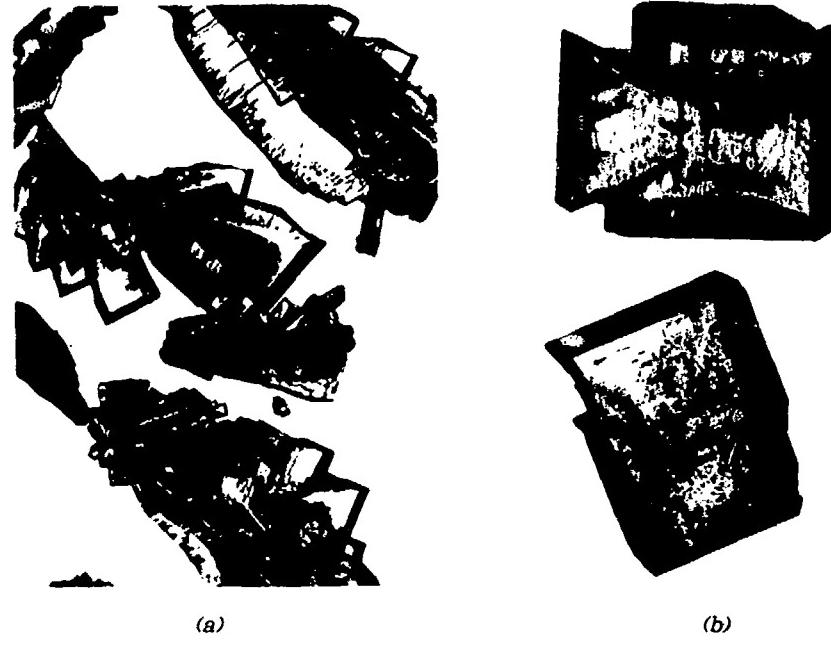


Figure 2 NTO recrystallised from water with addition of surfactant (X42).  
(a) 1% gelatin      (b) 1% methyl cellulose



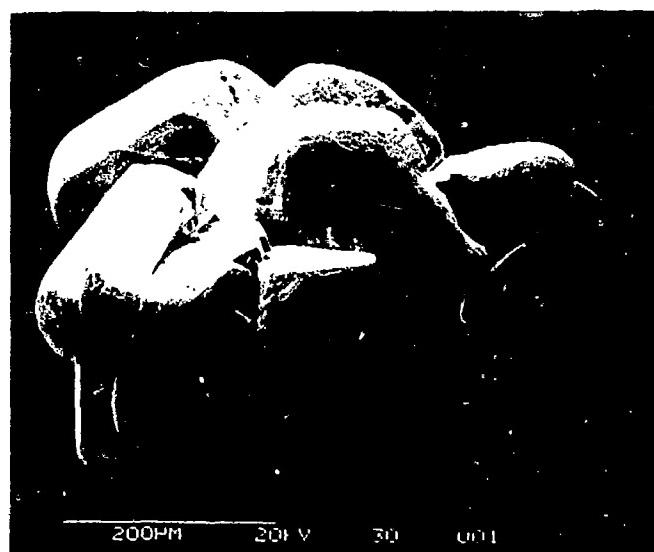
(a)

(b)

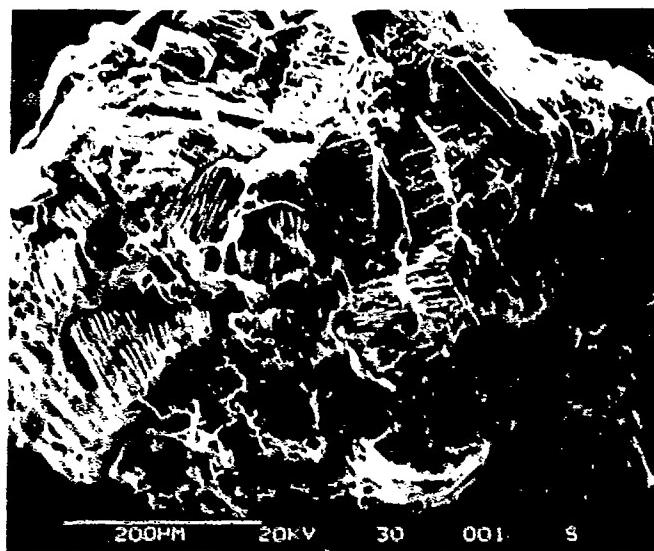


(c)

Figure 3 Photomicrographs of NTO formed during aqueous crystallisation (X42).  
(a) Bulk crystals obtained without stirring  
(b) Cubic crystals observed in the above crystallisation  
(c) Typical high bulk density NTO obtained during crystallisation with stirring



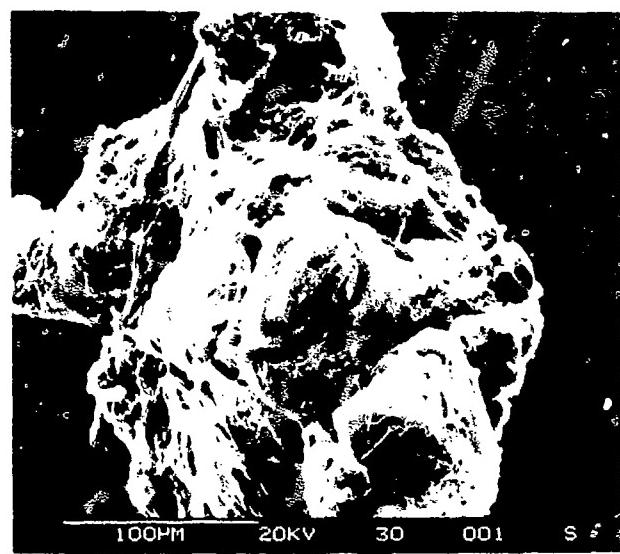
(a)



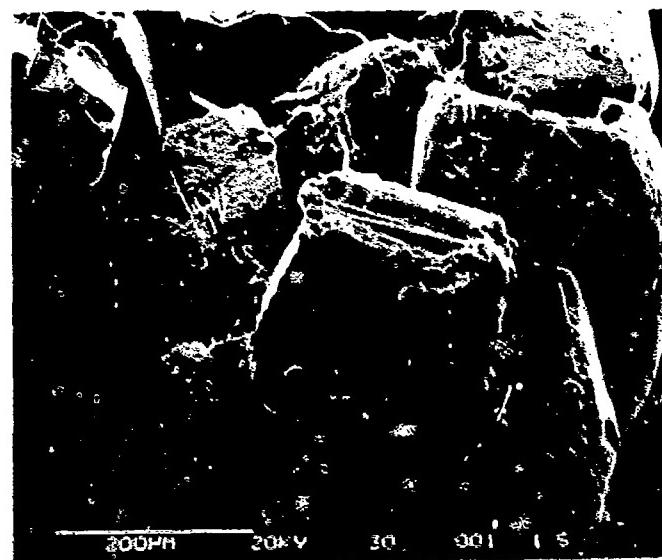
(b)

Figure 4 Scanning electron micrographs of NTO and polymer coated granules.

- (a) NTO crystals used for coating operations
- (b) NTO/Elvax 210 95:5
- (c) NTO/Elvax 650 95:5
- (d) NTO/Polyphosphazene 95:5



(c)



(d)

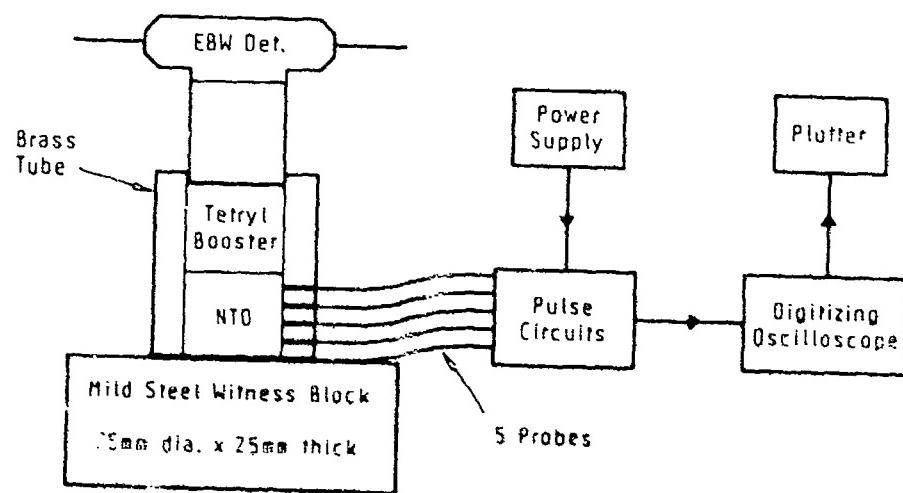


Figure 5 A Schematic Diagram of the Velocity of Detonation Measurement System

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## TITLE

A preliminary assessment of 3-nitro-1,2,4-triazol-5-one (NTO)  
as an insensitive high explosive

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## ABSTRACT

A simple two-step method to produce NTO in high yield from semicarbazide hydrochloride has been defined. A free-flowing material with bulk density ~ 0.9 g/ml has been produced by stirred aqueous recrystallisation; surfactants were ineffective in altering crystal habit. Impact sensitiveness of NTO was higher than expected although apparent propagation ability is low. Ignitability under thermal and electrostatic stimuli is substantially lower than RDX. Experimental firings were conducted to assess explosive performance for charges pressed to about 90 %TMD; velocity of detonation at 12.7 mm and 15.9 mm diameter was determined while detonation pressure (plate dent) and critical diameter were estimated. Performance at these diameters is somewhat lower than RDX. Moulding powders for 95:5 NTO:binder formulations were prepared from three commercial EVA resins and a flame retardant polyphosphazene. All three NTO/EVA formulations were insensitive to impact. Recommendations for continuing studies on insensitive booster formulations have been made.

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